

1.135.681



## PATENT SPECIFICATION

NO DRAWINGS

1.135.681

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## COMPLETE SPECIFICATION

## Process for preparing Aluminium-Amides and Derivatives thereof

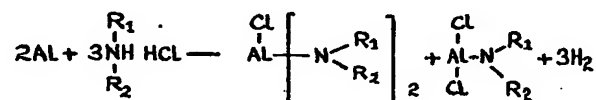
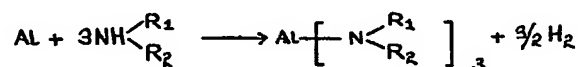
We, SNAM PROGETTI S.p.A., a body corporate organized under the laws of Italy, of Corso Venezia, 16, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to the preparation of unsubstituted or substituted aluminium-amides. 5

The preparation of aluminum-amides by reacting secondary amines and aluminum-alkyls (Belgian patent No. 592,417) or aluminum hydrides (J. Am. Chem. Soc., 82, 1960), pp. 2141—2144 is known.

10 These processes of preparation, due to the inherent characteristics of the reactants (aluminum alkyls and hydrides) require particular expedients for their performance and the required reaction temperatures are quite high. 10

15 It has now been found that aluminum-amides and halogenated derivatives thereof may be obtained by merely reacting activated metallic aluminum with primary or secondary amines and/or hydrohalides thereof, the reaction patterns being as follows: 15



20 in which R<sub>1</sub> is a hydrogen atom or a hydrocarbon radical, and R<sub>2</sub> is a hydrocarbon radical. Preferably the reaction is carried out in the presence of an inert hydrocarbon solvent. 20

While this reaction is particularly advantageous with secondary amines, to which reference will be made in this specification without implying any limitation thereto, it can nevertheless be employed, with certain particular expedients, also when primary amines are involved.

25 Aluminum-amides are useful as co-catalysts or catalysts in polymerization reactions and also as intermediates for the preparation of polymerisation co-catalysts and other aluminum derivatives. 25

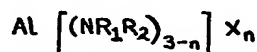
The reaction between the aluminum and the amine takes place within a temperature range between 80°C and 240°C, preferably between 120°C and 200°C.

30 It is possible to work also in the presence of catalytic amounts of hydrohalic acids, or, alternatively, an amine hydrohalide can be directly employed in catalytic amounts. 30

[Price 4s. 6d.]

If the amount of hydrohalide employed is considerable, an aluminum halogen-amide is obtained besides aluminum triamide.

The reaction between aluminum and amine hydro-halides is conducive to the formation, in predominant amounts, of aluminum halogenamides having the general formula:



in  $\text{R}_1$  and  $\text{R}_2$  are as defined above and  $\text{X}$  is a halogen atom,  $n$  being 0, 1 or 2.

In all of these reactions pure aluminum should be used, having a purity not less than 99%.

During the reaction, grinding of aluminum is effected, as a general rule, so as to increase the reactivity thereof. When the aluminum used as the reactant is not finely divided, or is deprived of activating substances, the grinding during progress of the reaction is critical to the end of causing the reaction to proceed at an adequate velocity.

The above reaction can be performed in the presence of solvents having a boiling point higher than the desired reaction temperatures and which are inert towards the reaction products.

It is advantageous to operate under pressure within rotary horizontal autoclaves which contain steel balls to ensure grinding.

The recovery of the expected reaction products is carried out with the procedures which are conventional in the art for this kind of reactions and compounds.

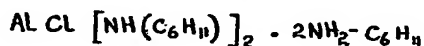
The examples to follow are intended as being merely illustrative of the invention, without any implied limitation thereof.

#### EXAMPLE 1

A 500-ml. rotary autoclave, containing steel balls, is charged with 65 g. cyclohexylamine hydrochloride, 250 mls. cyclohexylamine and 23 g. of granulated aluminum (325 Tyler), and heated for 2 hrs. at 130°C—140°C. Upon cooling a residual pressure of 98 atmospheres is observed, which corresponds to the reaction of about 20 g. aluminum. The reaction mixture is discharged and filtered. Only slight traces of Al are found in the filtrate. The residue is evaporated to dryness and thoroughly extracted with diethyl ether for 30 hrs. The evaporation of the extract yields 208 g. of a product in which:



Said product is ground in a ball mill in 500 mls. of anhydrous petroleum ether, then filtered and evaporated to dryness. The analysis corresponds to the formula

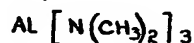
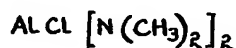


#### EXAMPLE 2

A rotary autoclave, containing steel balls and having a 500-ml. capacity is charged with 23.2 g. granulated Al (325 Tyler), 32.6 g. dimethylamine hydrochloride and 100 grs. anhydrous dimethylamine, and heated for 2 hrs. at 120°C—130°C.

Upon cooling, a pressure of 82 atmospheres is observed, which corresponds to 18 g. of reacted aluminum.

The reaction mixture is diluted with petroleum ether, discharged, filtered and the filtrate evaporated to dryness. A yellow product is obtained, which melts at 20°C (approx.) and is quantitatively distilled at 60°C—75°C (0.025 Torr.). The results of the analysis correspond to a 2:1 mixture of the following products:

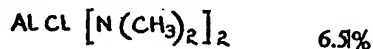


## EXAMPLE 3

By adopting the same implementation of the preceding example, 23 g. granulated Al (325 Tyler), about 160 g. dimethylamine and 4.2 g. dimethylamine hydrochloride are heated at 125°C—150°C for 2 hrs.

5 Upon cooling a pressure of 115 atmospheres is observed, which corresponds to 20 g. of reacted aluminum. 5

122 g. of a white crystalline product are obtained, whose analysis indicates the following composition:

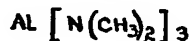


## EXAMPLE 4

A rotary milling autoclave is charged with 23.5 g. granulated aluminum (325 Tyler), 24 g. dimethylamine and 120 mls. anhydrous benzene, and heated up to 190°C for 7 hrs.

15 Upon cooling, the pressure observed is 23 atmospheres, corresponding to 6.0 g. of reacted aluminum. 15

A white product is obtained, entirely consisting of:



## EXAMPLE 5

20 An autoclave similar to the one employed in the preceding example is used, but without milling action. 20

23.5 g. of granulated alumina (325 Tyler), 23 g. dimethylamine, and 200 mls. anhydrous benzene, are heated at 199°C during 8 hrs.

25 Upon cooling no pressure increase, due to hydrogen evolution, is noted. 40 mls. of a benzene solution of HCl are then introduced and the mixture is heated for 2 hrs. between 178°C and 202°C. The pressure observed upon cooling is 20 atmospheres, corresponding to 5 g. of reacted aluminum. The product is nearly entirely: 25



## EXAMPLE 6 (Comparative)

30 A milling autoclave having a capacity of 2,000 mls. is used. 30

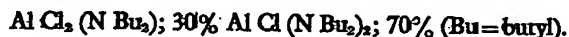
27 g. of oxidized powdered aluminum ("ALCOA"\* 408); 25 g. dimethylamine and 400 mls. anhydrous benzene are heated for 15 hrs. at 180°C—190°C. Upon cooling, no pressure increase is noted. It can be seen that the purity of aluminum is a critical factor to enable the reaction to take place.

## EXAMPLE 7

35 The following ingredients are heated for 4 hrs. between 180°C and 200°C in a milling autoclave: 35

40	Granulated aluminum (325 Tyler)	4.3 g.	
	Dibutylamine hydrochloride	11.8 g.	
	Dibutylamine	125 mls.	40

45 Upon cooling, a pressure of 7 atmospheres is noted, corresponding to 1.6 g. of reacted aluminum. The reaction mixture is discharged and filtered, the residue being metallic aluminum. The solution is evaporated to dryness, yielding a tarry, untandy product. In the light of the analysis of Al and Cl, the following approximate molar composition can be surmised: 45



\*The word "ALCOA" is a registered Trade Mark.

**WHAT WE CLAIM IS:—**

1. A process for the preparation of an aluminum amide or an aluminum-halogen amide which comprises reacting activated metallic aluminum which has a purity of not less than 99%, with at least one primary or secondary amine or a hydrohalide thereof at a temperature of from 80°C to 240°C. 5
2. A process as claimed in claim 1 in which the aluminum is activated by adding a catalytic amount of a hydrohalic acid or an amine hydrohalide into the reaction system.
3. A process as claimed in claim 1 in which the aluminum is activated by grinding it during the progress of the reaction. 10
4. A process as claimed in claim 1 in which the activated aluminum is finely divided aluminum.
5. A process as claimed in any of the preceding claims in which the reaction is carried out under autogenous hydrogen pressure.
6. A process as claimed in any of the preceding claims in which the reaction is carried out in the presence of an inert hydrocarbon solvent. 15
7. A process for the preparation of an aluminum amide or an aluminum halogen amide according to claim 1 and substantially as hereinbefore described with reference to Examples 1 to 5 and 7.
8. An aluminum amide or an aluminum halogen amide whenever produced by the process claimed in any one of the preceding claims. 20

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